Ab initio simulations of liquid systems: Concentration dependence of the electric conductivity of NaSn alloys

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Liquid NaSn alloys in five different compositions (20, 40, 50, 57 and 80% sodium) are studied using density functional calculations combined with molecular dynamics (Car-Parrinello method). The frequency-dependent electric conductivities for the systems are calculated by means of the Kubo-Greenwood formula.

The extrapolated DC conductivities are in good agreement with the experimental data and reproduce the strong variation with the concentration. The maximum of conductivity is obtained, in agreement with experiment, near the equimolar composition.

The strong variation of conductivity, ranging from almost semiconducting up to metallic behaviour, can be understood by an analysis of the densities-of-states.

During the past decades much work has been performed to investigate binary alloys, among which the so-called Zintl systems are of special interest. One typical example of these Zintl systems are alloys made of alkali metals and elements of the fourth group of the periodic table. In the last years much effort was made to investigate these systems in the liquid phase not only experimentally but also theoretically. One of the most successful theoretical tools to describe and interpret experimental findings is to perform *ab initio* molecular dynamics (MD) simulations for the particular systems. From the obtained trajectories one can extract data such as different structural and electronic properties of the liquid alloys. These results can be compared directly with experimental data.

Detailed investigations have already been performed for some Zintl alloys, such as K-Si [1], equimolar NaSn [2], Li-Si [3] and Cs-Pb [4]. However, these investigations were limited to only one composition. In a recent paper [5] we extended the investigation of the liquid NaSn alloys to a wide range of compositions ranging from 20% up to 80% of sodium. *Ab-initio* MD allowed to simulate the change of structural properties in these systems and made possible to discuss the static structure factors and the behaviour of the Zintl anions (Sn_4^{4-}) in the liquid phase. [5].

After the analysis of the structural properties, we have undertaken a detailed study of the electronic properties of these alloys and in the present letter we report the main results of such an analysis. In particular, we have calculated the electric conductivity as function of composition by averaging the Kubo-Greenwood formula [6] over the MD trajectories obtained in [5].

In the present study for the first time, we analyze, by means of computer simulation, the strong variation of the conductivity - ranging from metallic to almost semiconducting behaviour - with concentration. To get more insight into the electronic properties, we evaluated the electronic density of states and analyzed its specific atomic contributions.

We will start with the description of the methodology. After that, the results are presented. Finally a summary and outlook is given.

The MD simulations discussed in this paper were performed using the Car-Parrinello method [7] applying the MOTECC-90 computer code [8].

The considered systems consist of 64 atoms in a cubic unit cell with a length of 23.4 a.u. and periodic boundary conditions. The plane-wave cut-off was chosen to be 6 Ryd which we have justified by tests for dimers and bulk systems [5]. We used the pseudopotentials of Bachelet et al. [9].

The data for our analysis were collected from "production runs" of approximately 10000 steps each, corresponding to a total simulation time of about 2 ps. The temperature for each simulation was about 50 K above the experimental liquidus curve in the phase diagram.

For a more detailed description of computational features and the simulation

procedure (including systems and temperatures) see [5, 10].

The electric (AC) conductivity for a single configuration of the considered systems is obtained using the Kubo-Greenwood formula [6]:

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_m^{occ} \sum_n^{unocc} \sum_\alpha |\langle\psi_m|\hat{p}_\alpha|\psi_n\rangle\rangle|^2 \cdot \delta(\varepsilon_n - \varepsilon_m - \hbar\omega),$$

where m and e are the electronic mass and charge, respectively. Ω is the MD cell volume and $\hat{p}_\alpha$ is the α component of the momentum operator. The sum over m and n are respectively over the occupied and unoccupied states corresponding to the one-particle eigenvalues ε_m and ε_n. The extrapolation $\omega \to 0$ gives the DC conductivity.
In principle, to evaluate the thermal average of $\sigma(\omega)$, one should average the values obtained for all the configurations of an MD trajectory. However, this is not necessary, because consecutive time steps correspond to highly correlated configurations. Therefore, a significant saving of computational time can be gained if the configurations used to perform the average are spaced (well "separated") in time. The separation between each selected configuration should be large to ensure statistical independence between the configurational contributions to the average. We have chosen to perform a more drastic reduction of the contributions to the average due to the very heavy demand of the calculation of $\sigma(\omega)$ - taking in mind that the need of computing time is high since the evaluation of the Kohn-Sham states required by the Kubo-Greenwood formula was performed for a large number of states (200). In particular, we chose a time interval between configurations such that the mean squared displacement of the ions is about the size of the nearest-neighbour distance. For our cases it was sufficient to take into account $\sigma(\omega)$ for 6 geometries for each composition. We think this number of configurations should be considered as reasonable for a first analysis. Future work should exploit the possibility of performing calculations for a small set of empty states *on the fly* when the MD simulation runs. This type of calculations should be possible also within LCAO schemes.

To interpret the strong dependence of the conductivity from composition we calculated the averaged density-of-states (DOS) considering the same configurations as described above for each case. The electronic DOS has been evaluated using the same description of the electronic states as in the Car-Parrinello (plane wave expansion) MD calculations and also in a more approximate way by using a simplified LCAO-DFT method [11]. However, at variance with the plane wave expansion, the LCAO method allows to split in a rather unambiguous way the total DOS into fractions (i.e. partial densities-of-states) referring to the sodium and tin atoms, respectively.

The AC conductivity $\sigma(\omega)$ obtained for one representative composition is given in Fig. 1. The obtained curves $\sigma(\omega)$ indicate that the frequency dependence is non Drude-like witnessing the non-free electron like nature of the electronic states. For the extrapolation towards $\omega \to 0$ the data for small ω must be handled carefully. As in this region the denominator in the Kubo-Greenwood formula becomes very small and the statistical noise is very high, the error in the low frequency part is considerably large (cf. the discussion in [3]). In Fig. 1 the extrapolated value of $\sigma(0) = \sigma_{DC}$ is marked by a triangle. The statistical error of the calculated resistivity $\rho = 1/\sigma(0)$ is for each case about ± 100 $\mu\Omega$cm.

Fig. 2 shows our calculated resistivities in comparison with the experimental figures by van der Marel et al. [12], which have been measured for 70 K above the liquidus. As can be seen, the agreement is, within the statistical error, very good. The only exception is the composition with 80 % tin; however, the trend to a small (metallic) resistivity is obtained correctly for this case. For the discussion of this agreement it should be noted that one has also (i) approximations underlying the usage of the Kubo-Greenwood formula generally [6] and (ii) small differences between the experimental and theoretical temperatures (see above) and densities [5].

The most important result is the faithful reproduction of the variation of the resistivity with the composition shown by the experimental data.

This strong dependence of the conductivity on the composition can be understood qualitatively considering the densities of states. This discussion will be given in detail in a forthcoming paper [10]. Here we only summarize the essential results: The DOS splits up into contributions from the components (Na, Sn) of the alloy. Both contributions are well separated in energy (due to the atomic Kohn-Sham energies of sodium and tin): The low-energy region is dominated by tin, whereas for high energies sodium becomes dominant.

For compositions with a small content of sodium the Fermi energy lies in the region dominated by tin. This corresponds to a high DOS and therefore to a high (metallic) conductivity.

For compositions with 50 and 57% sodium the Fermi level is out of the tin-dominated region, but still has not reached the sodium-dominated area. This yields a small DOS for these cases at the Fermi level. Therefore, one gets an explanation for the minimum of the conductivity near the equimolar composition, as can be seen in Fig. 2. Analogously, for solid equimolar β-NaSn even a gap at the Fermi level (between two sets of states dominated by tin and sodium, respectively) was reported in literature [13].

In compositions with excess sodium the situation changes again: The Fermi level is in the sodium-dominated region, yielding again a metallic behaviour - similar to the tin-rich cases.

The observed behavior of the DOS is consistent with the theoretical analysis proposed by Geertsma [14] some years ago for these systems. A more detailed comparison between our simulation data and Geertsma's analysis is in progress.

We have determined the electric conductivities of liquid Na-Sn alloys for five different compositions with the Kubo-Greenwood scheme, using the trajectories from our *ab initio* MD simulations. The calculated values reproduce the measured strong variation of the conductivity with the Na (or Sn) concentration very well. The semiconductor-like conductivity of the alloys with 40...60% Na can be understood by considering the behaviour of the densities-of-states.

Our calculations were performed for temperatures about 50 K above the liquidus. However, the experiments [12] yielded also a considerable temperature dependence of the conductivities in the liquid and in the solid phases [15]. Hence, it is desirable to consider also (i) the T dependence of the conductivity for the liquid alloys, (ii) the conductivities of the solid phases, in particular, for the equimolar case [15]. Such investigations will be a subject of our future work.

In addition, we are going to consider larger supercells to investigate the effects of the finite supercell using the above-mentioned LCAO scheme [11].

Acknowledgements

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Figure captions

Figure 1: $\sigma(\omega)$: AC conductivity $\sigma(\omega)$ for the composition with 50% tin calculated with the Kubo-Greenwood formula. The plot represents an average over six configurations taken from *ab initio* MD simulations.
The extrapolated value for the DC conductivity is indicated by a triangle.

Figure 2: Calculated resistivities $\rho = 1/\sigma(0)$ (dots) with error bars (resulting from the extrapolation and from the configuration average) compared with experimental values (solid line) by van der Marel et al. [12] referring to systems 70 K above the liquidus.